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Pitto, Valentina; Voit, Brigitte I.; Loontjens, Ton J.A.; Benthem, Rolf A.T.M. van

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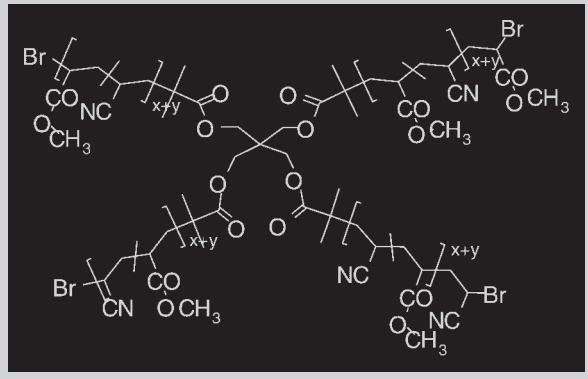
Summary: Atom transfer radical polymerization (ATRP) has been chosen as ''living''/controlled free radical polymerization system to synthesize a number of novel poly(acrylonitrile) (PAN) architectures. The reaction conditions for the synthesis of linear samples with control over molar mass and molar mass distribution have been investigated together with the possibility of obtaining copolymers of acrylonitrile with small quantities of methyl acrylate (max. 5 mol-%). Well-defined star polymers with 3, 4 and 6 arms have been successfully synthesized together with linear chains initiated by a bifunctional initiator and star-branched polymers with a hyperbranched poly(ester amide) as core. Molar masses were determined by NMR and GPC with the latter leading to a significant over estimation. Solution viscosity studies indicated that the stiff structure of the PAN chains is still maintained in the homopolymer star architectures and that the incorporation of small quantities of methyl acrylate as comonomer has a stronger effect on chain flexibility than the incorporation of star-branch points.



New Star-Branched Poly(acrylonitrile) Architectures: ATRP Synthesis and Solution Properties

Dedicated to Professor *Oskar Nuyken* on the occasion of his 65th birthday

Valentina Pitto,[1] *Brigitte I. Voit,**[1] *Ton J. A. Loontjens,*[2] *Rolf A. T. M. van Benthem*[2]

[1] Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany
E-mail: voit@ipfdd.de
[2] DSM Research, P.O. Box 18, 6161 MD Geleen, The Netherlands

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Introduction

Poly(acrylonitrile) (PAN) is a technical polymer with many applications – thanks to its high chemical and mechanical stability and its barrier properties to oxygen and carbon dioxide. In addition, due to the polarity of the nitrile groups, it is compatible with certain polar substances.[1] On the other hand it is not soluble in its monomer, which means that the synthesis on industrial scale has to be performed in a solvent with evident problems and costs for the waste disposal. In addition, it undergoes decomposition before reaching the melting point, which prevents melt processability. This fact considerably reduces the potential of poly(acrylonitrile) not only regarding injection moulding, but also for other possible applications, as, for example, melt coatings, where the ability of the material to flow is required.

Investigations regarding the properties of branched and hyperbranched polymers have shown that such structures have generally lower solution and melt viscosity compared with their linear analogues.[2] Therefore, in general one possible approach to enhance the rheological behavior of a polymeric material is to introduce branching points in the structure, or to add small quantities of highly branched macromolecules that are able to reduce the viscosity of the bulk material. Another possibility to specifically increase the melt processability of poly(acrylonitrile) is the introduction of an appropriate comonomer in the polymer chain.[3–5]

One way to introduce branching points in a polymer is to realize star shaped architectures. By changing the central, multifunctional core one can select the number of arms (and therefore number of branching points), as well as the chemical and physical properties of the whole molecule (by

varying the nature of the core). The most common synthesis method for industrial production worldwide is conventional free radical polymerization because of its straightforward feasibility, but generally such mechanism does not allow the obtainment of star polymers, because of the high number of radicals in the system that lead to cross-linked substances.

The development of ''living''/controlled free radical polymerization systems in the last years has highly increased the tools for the achievement of polymers with low polydispersity, tailored molar mass and controlled structures.[6–8] Among these systems, ATRP (atom transfer radical polymerization) is particularly attractive for the synthesis of novel and complex architectures[9–12] in rather straightforward operating conditions. Several groups[13–17] reported already on the synthesis of poly(acrylonitrile) using different controlled radical polymerization techniques and achieving narrow polydispersity, block copolymer formation and reasonable but still limited molar masses. However, only marginal attention has been given to the preparation of star like PAN architectures.[18]

With this article we would like to illustrate the strategies used to synthesize novel branched star-like poly(acrylonitrile) architectures using ATRP and to discuss the influence of the new structures on the polymer properties, with particular regard to solution viscosity.

Experimental Part

Materials

When not specified otherwise the chemicals have been bought and used without further purification (declared purity grade: *purissimum* $\geq$ 99%). Dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) from Fluka; *N*,*N*-diisopropylamine, benzoyl cyanide, anhydrous pyridine, 2-bromoisobutyryl bromide, pentaerythritol, dipentaerythritol, 2,2′-bipyridine, ethylene carbonate (purity: 98%) from Aldrich; 2-ethyl-2-hydroxymethyl-1,3-propanediol from Merck. Aldrich's copper bromide (CuBr) was purified according to the procedure of Keller and Wycoff[19] and stored under argon atmosphere at room temperature. The inhibitor was removed from Fluka's acrylonitrile (AN) by passing it through a neutral alumina column before each reaction. Methyl acrylate (MA) from Fluka was vacuum distilled over CaH_2 and stored a in dark flask under argon atmosphere at $-30\,^{\circ}C$. The hyperbranched poly(ester amide) Hybrane H-1 500[20] ($\overline{M}_n = 1\,500$ g/mol, $\overline{M}_w = 5\,500$ g/mol, PDI = 3.67, $T_g = 70\,^{\circ}C$, 7–8 average hydroxy functionalities) was received from DSM and used without further purification.

Measurements

The NMR measurements were performed with a Bruker DRX 500 NMR spectrometer at 500.13 MHz for ^1H NMR spectra and at 125.75 MHz for ^{13}C NMR spectra. DMSO-d_6 was used as solvent for all NMR experiments. The solvent peaks of DMSO were used as internal calibration: δ (^1H) = 2.50 ppm; δ (^{13}C) = 39.70 ppm; δ (^1H) = 2.50 ppm. The assignments of the signals are given in Scheme 2 and 3. SEC has been performed in DMAc (+2 vol.-% H_2O and 3.0 g/l LiCl) with Zorbax PSM 60, 300 and trimodal-S columns with a flow rate of 0.5 ml/min and a Knauer RI-detector. Linear poly(vinyl pyridine) has been chosen as standard. Viscosity measurements in DMSO (Fluka, absolute, $H_2O \leq 0.01\%$) were performed at 25 °C, using a Ubbelohde viscosimeter from Schott (capillary thickness ''*I*''; correction constant $k = 0.01007$). Thermal analysis were carried out with a DSC 7 instrument from Perkin Elmer with heating and cooling rates of 20 K/min. GAMESS and GROMACS 3.0.5 (University Gröningen, Molecular and Mesoscopic Dynamics Group, NL) softwares with basic sets 6-31G and STO-6G have enabled molecular modeling in a DMSO solvent box.

Synthesis of N,N-Diisopropylbenzamide [21]

N,*N*-Diisopropylamine (1.34 g, 10 mmol) was dissolved in about 30 ml dichloromethane and the solution was cooled to $-10\,^{\circ}C$. Benzoyl cyanide (1.31 g, 10 mmol) was dissolved in about 10 ml of the same solvent and added drop wise to the cooled solution. After removal of the solvent by evaporation, the product was subjected to column chromatography (SiO_2). Elution with a mixture of ether, methanol and THF (8:1:2) enables separation from the monomers. The product was obtained by evaporating the solvents and by drying in vacuum (4×10^{-3} mbar) over night at 40 °C. (yield: 93%, off-white crystals).

^1H NMR (ppm, DMSO-d_6): $\delta = 0.83$, 1.09 (s, anti and syn, 6H, H^8), ca. 3.5 (m, 4H, H^6), 3.74, 3.99 (s, anti and syn, 2H, H^7), 4.84 (s, 2H, H^9), 7.40 (m, 5H, $H^{1,2,3}$).

^{13}C NMR (ppm, DMSO-d_6): $\delta = 21.09$, 21.56 (s, anti and syn, C^8), 52.56, 57.06 (s, anti and syn, C^6), 64.11, 64.60 (s, anti and syn, C^7), 127.06 (C^3), 128.22 (C^2), 128.87 (C^1), 137.63 (C^4), 171.42 (C^5).

Synthesis of 2-Bromo-2-methylpropionic Acid 2-{Benzoyl-[2-(2-bromo-2-methyl propionyloxy)propyl]amino}-1-methylethyl Ester (2-arm-I)

N,*N*-Diisopropylbenzamide (2.61 g, 11 mmol) was dissolved under argon atmosphere in 40 ml anhydrous pyridine. To this 5 ml (ca. 40 mmol) of 2-bromoisobutyryl bromide were added drop wise at 50 °C over 15 min under vigorous stirring. After about half the amount had been added, pyridinium bromide precipitated. The reaction was complete after another 15 min stirring. At room temperature, 2 spoons of K_2CO_3 were added. After removal of pyridine by high vacuum condensation at $-196\,^{\circ}C$, the product was dissolved in chloroform and the rest of the pyridinium salts were removed by extraction with water. The obtained oil was subjected to column chromatography (SiO_2) to remove the 2-bromoisobutyryl bromide and the 2-bromoisobutyryl acid. Elution with a mixture of n-hexane and ethyl acetate (2:1) and evaporation of the solvents allowed the isolation of the product. (yield: 77%, yellow, viscous oil).

^1H NMR (ppm, DMSO-d_6): $\delta = 0.99$, 1.26 (s, anti and syn, 6H, H^8), 1.88 (s, 12H, H^{11}), ca. 3.7 (m, 4H, H^6), 4.97, 5.26 (s, anti and syn, 2H, H^7), 7.38, 7.45 (m, 5H, $H^{1,2,3}$).

^{13}C NMR (ppm, DMSO-d_6): $\delta = 16.96$, 17.10 (s, anti and syn, C^8), 30.28 (C^{11}), 58.32 (C^6), 70.36 (C^7), 79.31 (C^{10}),

127.01 (C^3), 128.55 (C^2), 129.66 (C^1), 136.24 (C^4), 171.31 (C^5), 172.51 (C^9).

Synthesis of 2-Bromo-2-methylpropionic Acid 2,2-Bis-(2-bromo-2-methylpropionyloxymethyl)butyl Ester (3-arm-I)

Under argon atmosphere 1.342 g (10 mmol) 2-ethyl-2-(hydroxymethyl)-1,3-propanediol were dissolved in 35 ml anhydrous pyridine. To this 7.5 ml (ca. 60 mmol) of 2-bromo-isobutyryl bromide were added drop wise at 50 °C over 15 min under vigorous stirring. After about half the amount had been added, pyridinium bromide precipitated. The reaction was complete after another hour stirring. At room temperature, 2 spoons of K_2CO_3 were added. After removal of pyridine by high vacuum condensation at −196 °C, the product was dissolved in chloroform and the rest of the pyridinium salts were removed by extraction with water. The product was obtained by evaporation of the solvent and purified by re-crystallization from chloroform. After washing with cold ethyl ether, the product was dried in vacuum oven at 60 °C over night. (yield: 19%, white crystals).

^{1}H NMR (ppm, DMSO-d_6): $\delta = 0.92$ (t, 3H, H^3), 1.55 (q, 2H, H^2), 1.90 (s, 18H, H^7), 4.15 (s, 6H, H^4).

^{13}C NMR (ppm, DMSO-d_6): $\delta = 7.48$ (C^3), 22.97 (C^2), 30.29 (C^7), 41.62 (C^1), 57.26 (C^6), 64.72 (C^4), 170.50 (C^5).

Synthesis of 2-Bromo-2-methylpropionic Acid 3-(2-Bromo-2-methyl-propionyloxy)-2,2-bis(2-bromo-2-methylpropionyloxymethyl)propyl Ester (4-arm-I)

Using the same procedure as for **3-arm-I**, 1.36 g (10 mmol) pentaerythritol and 10 ml (ca. 80 mmol) 2-bromoisobutyryl bromide were reacted (yield: 80%, white crystals).

^{1}H NMR (ppm, DMSO-d_6): $\delta = 1.91$ (s, 12H, H^5), 4.29 (s, 4H, H^2).

^{13}C NMR (ppm, DMSO-d_6): $\delta = 3.28$ (C^5), 43.05 (C^1), 57.18 (C^4), 63.27 (C^2), 170.39 (C^3).

Synthesis of 2-Bromo-2-methylpropionic Acid 3-[3-(2-Bromo-2-methyl-propionyloxy)-2,2-bis(2-bromo-2-methyl-propionyloxymethyl)propoxy]-2,2-bis(2-bromo-2-methylpropionyloxymethyl)propyl Ester (6-arm-I)

Using the same procedure as for **3-arm-I**, 3.814 g (15 mmol) dipentaerythritol and 24 ml (ca. 180 mmol) 2-bromoisobutyryl bromide were reacted (yield: 35%, white crystals).

^{1}H NMR (ppm, DMSO-d_6): $\delta = 1.90$ (s, 36H, H^6), 3.55 (s, 4H, H^1), 4.24 (s, 12H, H^3).

^{13}C NMR (ppm, DMSO-d_6): $\delta = 30.30$ (C^6), 43.69 (C^2), 57.24 (C^5), 63.48 (C^3), 69.20 (C^1), 170.38 (C^4).

Synthesis of Initiators with Hyperbranched Core

The average 7–8 hydroxy groups of Hybrane H-1500 were esterified with 2-bromo-isobutyryl bromide, aiming to obtain different degrees of substitution. Five macro-initiators with 2 to 6–7 bromine terminal groups were synthesized (25% to 80% –OH group substitution).

Selected sample (**Hyper-I-2**):

9 g (6 mmol) Hybrane H-1500 (ca. 45 mmol –OH) were dissolved under argon atmosphere in 40 ml anhydrous pyridine over night. 1.85 ml (ca. 15 mmol) of 2-bromoisobutyryl bromide were added drop wise at 50 °C over 15 min under vigorous stirring. After about half the amount had been added, pyridinium bromide precipitated. The reaction was complete after half an hour stirring. At room temperature, 1.5 spoons of K_2CO_3 were added. After removal of pyridine by high vacuum condensation at −196 °C, the product was dissolved in the minimum quantity of methanol and re-precipitated in cold water 3 times. The product was obtained by filtration and dried in vacuum oven at 60 °C over night. (yield: 35%, white powder). $\overline{M}_{n,(GPC)} = 1\,750$ g/mol, PDI = 4.65, $T_g = 71$ °C.

^{1}H NMR (ppm, DMSO-d_6): $\delta = 0.7–1.5$ (br m, $H^{6,6',11}$), 1.5–2.1 (br m, $H^{1,6,6',11}$), 1.88 (H^1), 2.5–3.0 (br m, H^{10}), 3.1–3.5 (br m, H^8), 3.6–4.0 (br d, H^5), 4.4–4.8 (br m, H^7), 4.8–5.3 (br m, H^4).

^{13}C NMR (ppm, DMSO-d_6): $\delta = 16–18$ (br, C^6), 20–22 (br, $C^{6'}$), 24–26 + 27–30 (br, C^{11}), 30.25 (C^1), 40–46 (br m, C^{10}), 48–57 (br m, C^8), 57.3 (C^2), 64–67 (br m, C^5), 67.5–74 (br m, C^4), 170.1 (C^3), 172–176 (br m, C^9).

Synthesis of Poly(acrylonitrile) and Poly(acrylonitrile-co-methyl acrylate) with ATRP

General Procedure (adapted from[14])

The inhibitor was removed from acrylonitrile (AN) by passing through an alumina column. CuBr and 2,2′-bipyridine (bipy) were added in a 100 ml Schlenk flask with ethylene carbonate (EC) and a magnetic stirrer. The flask was immersed in an oil bath at about 45 °C, and when EC was completely melted (mp = 37 °C), 2 cycles of vacuum-argon were performed. The temperature of the bath was raised to the desired reaction temperature, then AN and the initiator were added under argon atmosphere. Periodically, samples were removed from the reaction mixture and precipitated into THF. Then, they were washed with methanol and dried over night at 60 °C under vacuum.

Synthesis of the 6 Arm Poly(acrylonitrile) Star 6-arm-P-3 (Selected Sample)

Firstly, 0.0344 g (0.24 mmol) CuBr and 0.1123 g (0.72 mmol) bipy were dissolved in 35 g EC. Then 15 ml (0.224 mol) AN were added to the solvent and the temperature was raised to 75 °C. To this 0.092 g (4.8 mmol bromine functionalities) **6-arm-I** initiator were added and the reaction was performed for 2 hours. (yield: 30%, off-white powder). $\overline{M}_{n,(NMR)} = 16\,970$ g/mol, $\overline{M}_{n,(GPC)} = 40\,200$ g/mol, PDI = 1.74, $T_g = 95$ °C.

^{1}H NMR (ppm, DMSO-d_6): $\delta = 1.31$ (t, 3H, H^1), 2.04, 2.16 (br, H^3), 2.56–2.65 (m, 2H, H^5), 3.00 (br, 1H, H^2), 3.12–3.16 (br, H^4), 5.14–5.27 (m, 1H, H^6).

^{13}C NMR (ppm, DMSO-d_6): $\delta = 17.01–17.58$ (m, C^1), 22.78, 23.33 (C^2), 25.05–25.99 (m, C^6), 26.80/27.42/27.90 ($C^{4mm/4mr/4rr}$), 32.69 (m, C^3), 36.07 (br, C^5), 117.36–117.70 (m, $C^{6'}$), 119.69 (t, $C^{4'rr}$).

Synthesis of the 4 Arm Star Copolymer 4-Arm-CP-5 (Selected Sample)

Firstly, 0.0344 g (0.24 mmol) CuBr and 0.1123 g (0.72 mmol) bipy were dissolved in 22.5 g EC. Then 9.65 ml (0.144 mol) AN were added to the solvent and the temperature was raised to 75 °C. To this 0.65 ml (7.2 mmol) methyl acrylate and 0.088 g (0.48 mmol bromine functionalities) **4-arm-I** initiator were added rapidly one after the other and the reaction was performed for 2 h. (yield: 27%, off-white powder). $\bar{M}_{n,(NMR)} = 23\,080$ g/mol, $\bar{M}_{n,(GPC)} = 32\,500$ g/mol, PDI = 1.61, $T_g = 96$ °C.

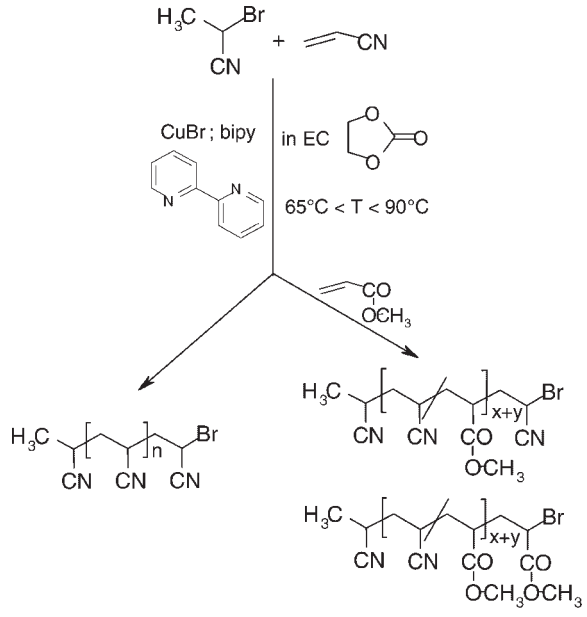
^{1}H NMR (ppm, DMSO-d_6): $\delta = 1.20$, 1.24 (br d, 24H, H^5), 1.90 (br shoulder, H^7), 2.04–2.15 (br, H^6), 2.53–2.65 (m, H$^{13'}$), 2.77 (br, H^{13}), 2.91 (br shoulder, H^7), 3.12–3.17 (br, H^{11}), 3.68, 3.70, 3.71 (m, H^9), 3.75 (s, H^{16}), 4.11, 4.21 (br d, 8H, H^2), 4.50–4.80 (m, H^{14}), 5.13–5.28 (m, H$^{14'}$).

^{13}C NMR (ppm, DMSO-d_6): $\delta = 23.43$, 23.74, 23.86, 25.84, 26.14 (m, C^5), 25.04, 26.02 (m, C$^{14'}$), 26.86/27.47/27.96 (C$^{11mm/11mr/11rr}$), 32.47–33.22 (m, C^{10}), 33.41–34.37 (br m, C^6), 35.05–35.46 (br m, C$^{13'}$), 36.15 (br, C^{13}), 40.84 (C^1), 41.07 (br, C^7), 41.46–41.55 (m, C^4), 42.21, 43.43 (m, C^{14}), 52.02, 52.09, 52.17 (m, C^9), 53.20 (br, C^{16}), 61.89 (br, C^2), 119.73 (t, C^{12rr}), 120.05 (t, C^{12mr}), 120.35 (t, C^{12mm}), 169.00 (br, C^{15}), 173.13–173.35 (m, C^8), 175.41 (br, C^3).

Results and Discussion

Generally, ATRP can be performed using different transition metals and halogens as catalyst systems. In our case bromine was chosen as halide atom in view of the fact that, combined with copper as transition metal, it allows the achievement of higher polymerization rates.[14] A first investigation of the reaction system was carried using 2-bromoproprionitrile as initiator for linear samples following results reported on controlled radical polymerization (ATRP) of AN by Matyjaszewski et al.[13,14] 2,2′-Bipyridine has proved to be the best ligand in the catalyst system for the obtainment of narrow molar mass distributions. The ratio between copper bromide and bipyridine has been set to 1:3. The reaction cannot be performed in bulk, due to the poor solubility of poly(acrylonitrile) in its monomer, nevertheless ethylene carbonate has confirmed to be an adequate solvent to perform the synthesis successfully (Scheme 1).

In the studies of Matyjaszewski[13,14] conversion degrees of acrylonitrile up to 95% have been reported. We were not able to reproduce these high values even after performing intensive studies to optimize the reactions conditions like temperature, reaction time and the ratios of the various components. The achieved conversion remained usually below 35%. We have to conclude that the reaction does not undergo a real ''living'' process even though narrow polydispersity could be achieved and the conversion corrected calculated molar masses agree well with the determined ones (e.g. **L-P-2**: $\bar{M}_{n,(NMR)} = 1\,600$ g/mol, PDI (SEC) = 1.04, 33% conversion, calculated $\bar{M}_n$ for 33% conversion = 1 655 g/mol): the chains grow up to a certain length

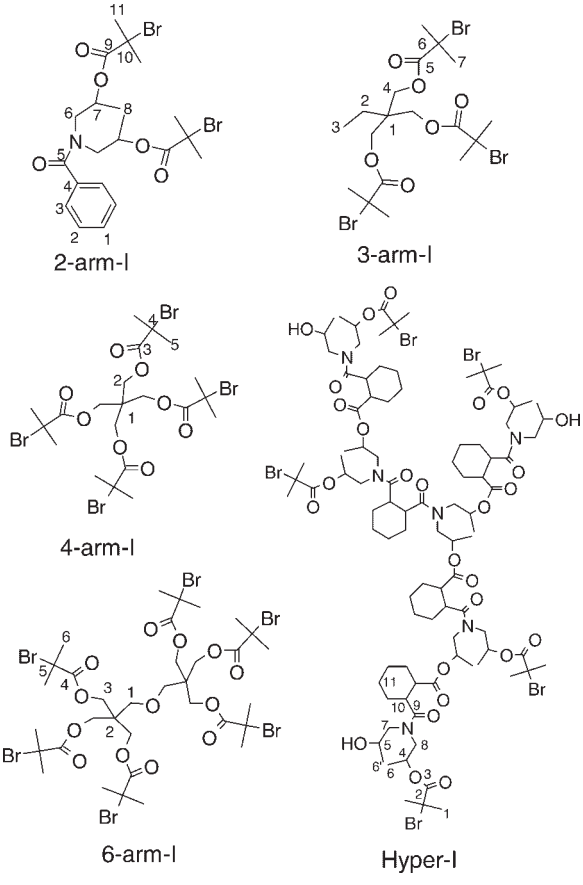


Scheme 1. Homo- and copolymerization of acrylonitrile by ATRP.

($\bar{M}_{n,(NMR)}$ max. 10 000 g/mol) and then are not able to develop any further even though the existence of the bromine end group can be verified. Also re-initiation with new or additional ligand/CuBr using again AN as monomer failed whereas successful chain extension experiments are reported when the monomer (e.g. to butyl acrylate) **and** the ligand system was changed.[15,17]

Interactions between the catalyst system and the isotactic sequences of the poly(acrylonitrile) growing chain are suspected to be responsible for such behavior. In fact, when we introduced small quantities (up to 5 mol-%) of methyl acrylate in the feed, reproducible conversion values up to 70–75% are achieved. The MA repetition units in the chain seem to be able to disturb the strong polar interactions between the nitrile groups and, consequently, the formation of complexes with the copper catalyst. In addition, analyzing the nature of the end groups in the copolymers from the NMR spectrum, one has to realize that 50% of the chains end with a bromine terminated methyl acrylate unit. This is not compatible with the small quantity of MA in the feed in case of statistical copolymerization, but can be explained by the difficulty of AN units to add to MA units and thus, an enrichment of MA units at the chain end. In fact, the group of Matyjaszewski has already reported[15,17] that PAN-poly(butyl acrylate) block-copolymers are easier to synthesize building the second block from PAN than the reverse chain extension of AN from poly(butyl acrylate).

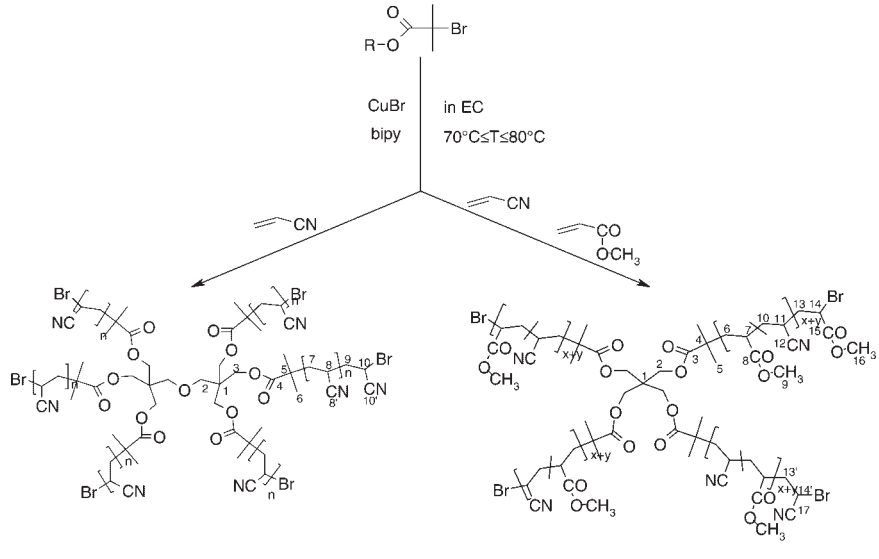
To synthesize well-defined star-like structures it is important to have fast and quantitative initiation from a well-known number of initiating sites. Such conditions allow the regular growth of a pre-determined number of chains. For these reasons well defined multifunctional



Scheme 2. Multifunctional initiators for atom transfer radical polymerization.

initiators have been synthesized by choosing suitable polyols and introducing bromine groups on their structures. The esterification of the hydroxy groups has been performed using 2-bromoisobutyryl bromide, applying the conditions adopted by Frey and co-workers.[22] The synthesized initiators are reported in Scheme 2. In addition, to the well defined, low molar mass initiators, also a polymeric hyperbranched multifunctional initiator was prepared on the base of the commercially available Hybrane (DSM product) which showed a broad molar mass distribution. Since this initiator (**Hyper-I**) contains amide units which might disturb the controlled radical polymerization and also because it is less well defined due to the broad molar mass distribution and therefore no conclusions can be drawn by following the molar mass distributions, the bifunctional initiator **2-arm-I** was synthesized to act as model initiator for **Hyper-I**. All the multifunctional structures have been successfully used to initiate the polymerization of acrylonitrile and to result in soluble products meaning cross-linking due to radical coupling could be avoided as expected from a working ATRP system. Examples of a 6 arm star and of a 4 arm copolymer star are reported in Scheme 3.

However, the reaction conditions had to be tailored for each initiator. After having selected ethylene carbonate as solvent and having set the ratio between copper bromide and 2,2′-bipyridine to 1:3, the reaction conditions have been optimized, depending on the number of functionalities and on the structure of the initiator. The optimized conditions concerning the reaction time and temperature as well as the ratios monomer/initiator and initiator/catalyst system are summarized in Table 1 together with the molar mass, PDI (polydispersity index) and conversion ranges achieved for every initiating system. Generally it could be stated that linear samples need much longer reaction times than branched ones to be synthesized and that the PDI increases with the complexity of the initiating structure. In addition, high conversion of acrylonitrile could not be reached in any system and single poly(acrylonitrile) chains are able to



Scheme 3. Synthesis of poly(acrylonitrile) homo- and copolymer stars.

Table 1. Optimized conditions for the synthesis of linear and star acrylonitrile polymers by atom transfer radical polymerization (solvent: EC, ligand: bipy, CuBr/ligand 1:3).

Samples	AN/-Br	-Br/CuBr	T	Time	$\bar{M}_{n,(NMR)}$	PDI GPC	$\bar{M}_{n,(GPC)}$	Yield
			°C	h	g/mol		g/mol	%
L-P	100–1 000	2–20/1	65–70	19–96	1 500–10 500	1.04–1.25	4 900–27 500	25–35
2-arm-P	100–1 000	1–5/1	70–75	1–22	5 000–18 000	1.15–1.35	7 900–28 800	20–30
3-arm-P	300–470	1–2/1	70–75	1–2	10 000–20 000	1.3–1.7	23 600–51 800	10–30
4-arm-P	200–470	1–5/1	70	1–5	2 500–20 000	1.2–1.5	6 600–50 000	10–25
6-arm-P	200–470	1–2/1	75–80	1–4	11 000–30 000	1.4–1.9	30 800–1 10 500	15–35
Hyper-P	200–1000	1–5/1	70–75	1–24	–	1.90–2.35	31 200–84 800	20–25
L-CP	50–470	2–20/1	90	20	2 000–5 500	1.13–1.50	2 300–13 700	50–75
4-arm-CP	200–470	1–2/1	75	1–2	8 000–32 000	1.45–1.65	12 500–48 000	20–30

grow only up to a certain length. This seems to be a particular feature in the controlled polymerization of acrylonitrile, in fact, also using other controlled systems as RAFT (radical addition fragmentation transfer polymerization), no PAN samples with NMR calculated molar masses higher than 5 000 g/mol[17] have been reported so far. Hawker and co-workers have been able to control the molar mass of PAN chains up to 50 000 g/mol using TEMPO derivatives,[16] but these $\bar{M}_n$ data have been obtained with GPC measurements and are not comparable with the ones calculated from the NMR spectrum.

With the exception of the Hybrane based systems, NMR measurements have enabled the full structural characterization of the synthesized architectures. The ^{1}H NMR spectra of each structure show both signals of the repetition unit (C<u>H</u>$_2$-CHCN and CH$_2$-C<u>H</u>CN), as well as all the peaks concerning the different initiating molecules and the bromine end groups (C<u>H</u>(CN)-Br) within the polymers. In general, the ratio between the initiator functions and the end groups was similar indicating that no bromine end group is lost during the reaction.

The ^{1}H NMR spectrum of a poly(acrylonitrile) star polymer (**4-arm-P-3**, selected sample) is reported in Figure 1. Splitting of the methyl and ethyl groups of the core molecule can be observed in the polymer spectra (signals **5** and **2**, respectively), due to the pro-chirality of the carbon atom between the 2 –CH$_3$ groups (**4**): the nitrile groups of the first two acrylonitrile units can be on the same side (conformation *mm*) or on opposite sides (conformation *mr*). Therefore, a mixture of 2 diastereomers coexists in the sample, and leads to the splitting of the signals. Compared to the **4-arm-I** initiator spectrum signal **5** also shifts towards lower fields (from 1.9 ppm to 1.2 ppm), due to migration of the bromine atom to the end of the chain. The end functions (C<u>H</u>(CN)-Br) can be detected at 5.1–5.3 ppm.

Both, proton NMR analysis and GPC (<u>g</u>el <u>p</u>ermeation <u>c</u>hromatography, also known as SEC, <u>s</u>ize <u>e</u>xclusion <u>c</u>hromatography) measurements were chosen to determine the equivalent or number average molar masses. GPC provided in addition information on the polydispersity of all synthesized samples. The use of an absolute method as NMR for the determination of an equivalent molar mass

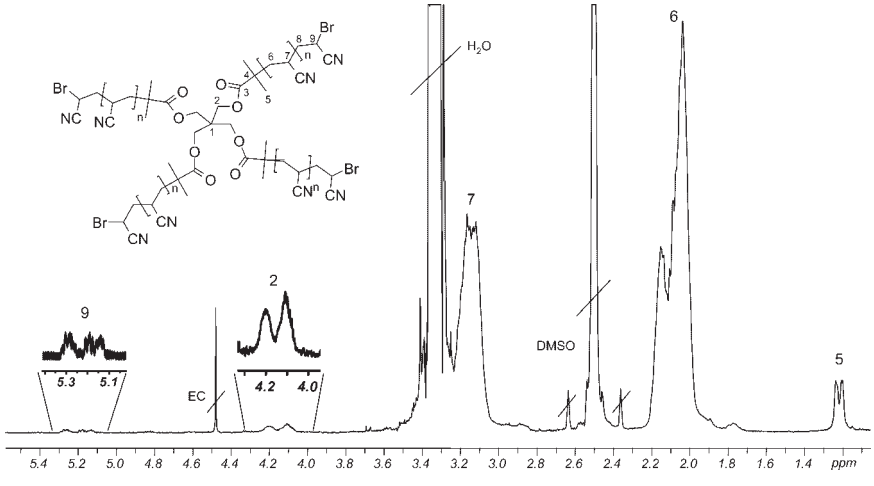


Figure 1. ^{1}H NMR spectra in DMSO-d_6 of the 4 arm poly(acrylonitrile) star **4-arm-3** (5 h, 70 °C, [AN]$_0$ = 4.22 M, [AN]$_0$/[Br]$_0$/[CuBr]$_0$/[bipy]$_0$ = 300/5/1/3; $\bar{M}_{n,(NMR)}$ = 9 660 g/mol, $\bar{M}_{n,(GPC)}$ = 19 850 g/mol, PDI = 1.21).

M_{NMR}, which can be regarded as a number average molar mass $\overline{M}_n$, was possible only because of the controlled/living character of the ATRP reaction, which allows the synthesis of well-defined architectures. Just in the case of definite structures the assignment of the end group signals in the spectra and the comparison of their integrals with the ones of the repetition units enables to determine the number of repetition units and therefore to calculate reliable values for the molar masses. In our case, both the bromine end groups and the methyl groups at the beginning of the chains can be identified and quantified, enabling a consistent calculation of M_{NMR}. Problems occurred however by the analysis of high molar mass samples and when the molar mass distributions broaden. Therefore the data on the 6 arm star products have to be evaluated with some care due to the larger error, and on the Hybrane based products no reliable quantification of the initiator content was possible and therefore, no molar mass values were calculated from NMR data.

GPC is a relative method and is generally calibrated with poly(styrene) as standard. However, due to the polarity of the nitrile groups in poly(acrylonitrile) and to the limited solubility, we measured GPC in DMAc and we decided to use poly(vinyl pyridine) (PVP) as standard, hoping for a higher similarity of the hydrodynamic radius and consequently for a better molar mass estimation.

Comparing the molar masses determined from GPC and NMR measurements (Table 2) one has to state that, independently on the architecture (linear or star polymers) and on the chemical composition (homo- or copolymers), the $\overline{M}_n$ values obtained with GPC are much higher than the ones obtained from the NMR spectra. This is an unexpected result, since in general it is assumed that star polymers have a more compact structure compared with their linear homologues, therefore the GPC determined $\overline{M}_n$ values should be underestimated. However in the case of PAN, the stiff structure generated from the polar character of the –CN groups is probably responsible for a rather high hydrodynamic volume of the macromolecules with consequent overestimation of the GPC calculated molar mass when flexible molecules as PVP are used for calibration.

Of course, the determination of the molar mass by NMR structure analysis may also not be free from error, because the number of repetition units determined from the NMR spectra depends on the integration limits, which are manually set. In addition, overestimation can occur when the –CH(CN)Br end group is taken as reference, because of some loss of bromine atoms at the end of the chain noticed during several experiments. For this reason the initiator signals have been chosen as reference for the integration, although this can lead to underestimation of the molar masses, when star-star coupling takes place. Despite the described possible error factors, no evident proof for such deviations could be found in our NMR analysis and therefore the NMR measured molar mass values have been considered as much more reliable than the GPC obtained ones throughout the work.

Comparing M_{NMR} and $\overline{M}_{n,(GPC)}$ the existence of a linear correlation between the values obtained from NMR and GPC experiments has been noted for the copolymers as well as for the homopolymers up to the 4 arm stars (Figure 2). For the 6 arm stars, no good correlation was achieved. This feature, together with the somewhat broader distribution of the molar masses determined for these samples, indicates the possibility of not complete initiating efficiency of the bromine groups of the 6 arm initiator, because of the increased sterical hindrance around the active sites. In this case not all the initiating sites start off a chain and the products seem to be a mixture of stars with 4 to 6 arms of different chain length.

Table 2. M_{NMR} and $\overline{M}_{n,(GPC)}$, PDI, yield and relative viscosity (0.5 wt.-% solution in DMSO, 25 °C) of selected linear and branched structures.

Sample	M_{NMR}	$\overline{M}_{n,(GPC)}$	PDI	Yield	η_{rel}
	g/mol	g/mol		%	
L-P-3[a)]	1 570	5 300	1.04	36	1.05
L-P-8	10 400	27 500	1.25	–[b)]	1.23
L-CP-2	2 050	5 650	1.21	50	1.05
L-CP-6	7 240	13 750	1.65	53	1.14
2-arm-P-4	7 180	19 200	1.17	–[b)]	1.13
3-arm-P-2	11 705	23 850	1.42	22	1.18
3-arm-P-3	21 265	51 850	1.72	29	1.50
4-arm-P-5	11 350	25 550	1.41	23	1.19
4-arm-P-8	19 720	50 000	1.31	25	1.34
4-arm-CP-1	8 120	12 500	1.50	9	1.10
4-arm-CP-2	12 610	22 450	1.45	20	1.16
6-arm-P-1	11 200	30 800	1.40	4	1.18
6-arm-P-4	17 620	67 900	1.77	37	1.27
Hyper-P-2	–[b)]	47 000	1.94	–[b)]	1.27

[a)] $\overline{M}_n$ value for 100% conversion 5 022 g/mol, $\overline{M}_n$ value at the achieved conversion 1 807 g/mol.
[b)] Not determined.

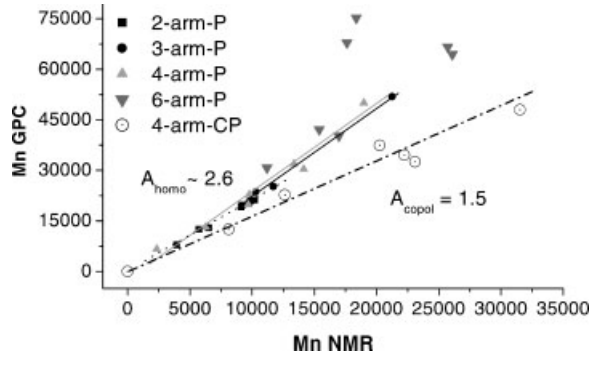


Figure 2. Correlation between number average and equivalent molar mass values obtained with GPC and NMR measurements.

Of particular interest was the comparison of the slope values (A) of the linear fits for the different architectures; in this case A can be looked at as:

$$A = \frac{\overline{M}_{\mathrm{n\,GPC}}}{M_{\mathrm{NMR}}} \quad (1)$$

Because of the dependence of GPC measurements on the hydrodynamic volume of the samples in the elution solvent (DMAc), the decrease of A means decrease of $\overline{M}_{\mathrm{n,(GPC)}}$ at equal M_{NMR} and could be an indication of a more coil-like structure. For nearly all the homopolymers we can state the existence of a quite constant ratio $\overline{M}_{\mathrm{n,(GPC)}}$:$M_{\mathrm{NMR}}$ of approximately 2.6. For the homopolymer sample obtained using the bifunctional initiator A is 2.0. The slight decrease of $\overline{M}_{\mathrm{n,(GPC)}}$ seems to point to a more coiled conformation of this architecture in DMAc. Probably the kink introduced by the initiating molecule in a basically linear structure influences the polar interactions between the pendent nitrile groups, diminishing the stiffness of the polymer. For the copolymers (linear and star) A is 1.5, which indicates a significant lower $\overline{M}_{\mathrm{n,(GPC)}}$ than for the homopolymers and consequently a more coiled conformation. This is a very interesting aspect, in fact the small quantity of methyl acrylate introduced among the acrylonitrile units seems to be able to disturb the rigidity of the polymer structure much more than the introduction of star branching points even though we had to state that the MA units are not randomly incorporated within the PAN chain.

Viscosity measurements in DMSO have been performed to investigate the properties of the new architectures in solution. The relative viscosity of homo- and copolymer samples with similar molar masses and different number of arms have been compared. In general, one can state that the copolymer η_{rel} are lower than the ones of the analogue homopolymers (even when the molar masses are higher), pointing to a smaller hydrodynamic radius in DMSO. When the molar masses are the same, the linear copolymer has higher viscosity than the star copolymer, indicating a more compact form for the latter. This is expected, because, if $\overline{M}_{\mathrm{n}}$ is the same for both samples, then each single arm must be about ¼ of the linear chain and the hydrodynamic volume cannot be identical. The presumed enhanced flexibility of the products obtained using **2-arm-I** as initiator mentioned above is confirmed by the viscosity experiments: their η_{rel} are lower than the ones of the linear homologues and of the linear copolymer samples. In general, lower viscosity values are expected for samples of similar molar masses, when the number of arms increases. Comparing 3, 4 and 6 arm (with special care!) stars, we can state that this is not the case for poly(acrylonitrile): the η_{rel} values are quite similar, and if any conclusion wants to be drawn, then the 4 arm stars seem to interact slightly better with DMSO than the 3 arm ones. The only exception is given by the star polymers with hyperbranched core, that have lower relative viscosity than the well-defined ones. On the other hand, these samples have a very broad distribution of the molar masses, a complex irregular structure mixture, and no reliable molar mass values could be obtained by NMR.

We concluded that the rather narrow molar mass distributions and the reliability of the molar mass values calculated from the NMR spectra at least for selected samples should allow the shape estimation of the new architectures in DMSO solutions using viscosity studies. Such prediction can be made usually by analyzing the form factors $\boldsymbol{\alpha}$, obtained with the Kuhn-Mark-Houwink-Sakurada equation.[23] In its double logarithmic expression, one can determine the constants $\boldsymbol{k}$ and $\boldsymbol{\alpha}$ (Figure 3):

$$\ln(\eta) = \ln \boldsymbol{k} + \boldsymbol{\alpha} \ln M \quad (2)$$

The experimental determined values $\boldsymbol{k}$ and $\boldsymbol{\alpha}$ are reported in literature for common polymers, and have to be found out for new polymers. To achieve information on the shape of polymers in solution, one has to focus the attention on $\boldsymbol{\alpha}$. Generally, low α values (<0.5) are expected for star-branched polymer structures, large $\boldsymbol{\alpha}$ values indicate a stiff polymer chain or are found e.g. in the case of polyelectrolytes when repulsive forces are present.

Since we have so far no reliable method to determine the weight average molar mass – unfortunately we were not able to perform light scattering experiments with our samples – we had to use our molar mass values from NMR analysis (near $\overline{M}_{\mathrm{n}}$) for the form factor evaluation studies. Therefore, the data given in the following should be considered a preliminary study and were only used to point out general tendencies. The relatively narrow molar mass distribution of the samples, however, helps to minimize the possible error.

The results of our investigation on some selected products where a sufficient high variety of samples of different molar masses were available are summarized in Table 3. Comparing the $\boldsymbol{\alpha}$ values for the 5 different polymers, one can notice that the linear and 2 arm poly(acrylonitrile) samples as well as the copolymers adapt in DMSO more or less a disturbed flexible coil-like shape with $\boldsymbol{\alpha}$ values in the range 0.6–0.8, while the 4 arm polymer star seems to adapt

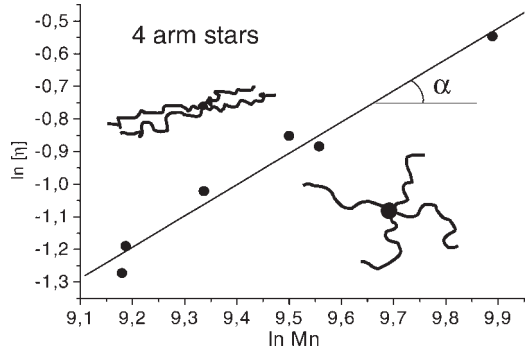
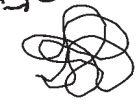


Figure 3. Mark-Houwink plot of the 4 arm poly(acrylonitrile) stars for the evaluation $\boldsymbol{\alpha}$ ($\boldsymbol{\alpha} = 0.96$).

Table 3. Form factors and shape prediction of the new poly(acrylonitrile) architectures.

Samples	α	Shape prediction	
		Viscosity measurements	Molecular modeling
Linear homopolymers	0.74		
2 arm	0.59		
4 arm stars	0.96		
Linear copolymers	0.70		
4 arm copolymer stars	0.67		

a disturbed stiff rod-like shape ($\alpha = 0.96$). Again, the 2 arm samples have a very small α, compared to the other polymers. This confirms that the linking unit introduced in a ''pseudo-linear'' chain by the bifunctional initiator effectively leads to more coiled molecules in solution. The slightly smaller α values of the linear copolymers compared to the linear homopolymer also support the thesis of higher chain flexibility of these architectures. The result on the 4 arm star homopolymer is surprising: an α value of about 1 indicates a shape between a disturbed flexible coil and a stiff rod. One would assume that the branching in the star molecules leads to a more compact structure and thus, lower α values for the branched structures compared to the linear ones, but this does not seem to be the case when acrylonitrile is chosen as monomer. Not much information is given in the literature on α values for this type of architectures: the statement that the polymers have a disturbed rod-like conformation when α is 1–2 derives only from the investigation of linear systems, therefore we do not know with certainty what high α values mean for these specific poly(acrylonitrile) architectures. An investigation performed by Goodson and Novak[24] states $\alpha = 1.14$ for 3 arm poly(n-hexyl isocyanate) stars. Of course, the comparison is only qualitative, because of the different chemical composition of the examined samples, nevertheless, as PAN, poly(isocyanate)s are characterized by rather stiff architectures due to the reorganization of the chain in an helical structure. Very pronounced, however, is the effect of MA comonomer on the 4-arm star structure: the α valued is reduced from 0.96 to 0.67 indicating finally a coiled conformation of the branch arms.

Due to the novelty of the synthesized architectures and the consequent lack of information about their behavior in solution, molecular modeling experiments of a 4 arm homopolymer star in a DMSO solvent box have been performed to cross-check the results obtained with the viscosity measurements. The arms of the simulated molecule stretch in every direction with an angle of circa 90° one from the other, pointing to a certain stiffness of the single arms and to a repulsion between the chains in the same polymer. No rod-like shape and no strong interaction between single poly(acrylonitrile) chains of the same star could be confirmed. This is why we can only say that the new PAN architectures exhibit a rather large hydrodynamic radius and we can suppose that their shape can vary from disk to rod-like, depending on how the stiff arms behave in DMSO.

Important information regarding the hydrodynamic radius and the geometry of complex macromolecular architectures can be obtained performing light scattering measurements. Unfortunately the poor solubility of poly(acrylonitrile) in general, and the limited availability of the new branched structures in particular, has hindered such investigations up to now. Thus, a more detailed study will be necessary to confirm our unusual findings regarding solution properties of these star polymers with stiff arms.

Finally, regarding the material properties, the introduction of branching points does not seem to improve considerably the solubility of poly(acrylonitrile), as would have been expected from observations regarding different polymer structures. Also, during thermal analysis of the bulk material no improved melting could be observed and T_g's were found to lie between 80 °C and 95 °C for all structures, without a clear trend. The copolymers show somewhat more distinct glass transitions, which are a sign of rheological softening, nevertheless complex polar interactions are still present and prevent the achievement of an adequate flow behavior.

Conclusion

To conclude, one can say that atom transfer radical polymerization is an efficient controlled radical method that enables the synthesis of new well-defined star-like branched poly(acrylonitrile) architectures: the termination events can be minimized and very good control over the end groups and the molar masses can be achieved, even if no linear increase of $\overline{M}_n$ over the full conversion range was observed. According to our investigation in the case of acrylonitrile it is no true ''living'' polymerization, since it stops without loosing the end groups when the chains reach a certain length. The introduction of branching points does not seem to change considerably the behavior of poly(acrylonitrile) in solution, as would have been expected from observations regarding other polymer structures. The relative viscosity of the branched samples is slightly lower

than the one of the linear ones, however the determination of the form factors points to a very stiff structure of the star PAN homopolymers in solution. On the other hand, the copolymerization of AN with small quantities of methyl acrylate leads to somewhat smaller form factors, indicating higher flexibility of the chain and the adoption of a more coiled conformation because of the decreased polar interactions. This is especially pronounced in the 4-arm star copolymer structure.

Finally we have to state, that star-branched polymers with stiff arms are a new and up to now not well understood class of branched macromolecules regarding their interactions in solution. Further studies involving light scattering experiments are certainly required. However, the possibility to prepare those structures with narrow molar mass distribution by controlled radical polymerization allows for the first time a more detailed look in solution properties and property evaluations based on molar mass dependencies. In addition, we could prove that even very complex star-like hybrid structures based on a broadly distributed multifunctional hyperbranched core and PAN arms can be realized by using ATRP techniques.

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